# Microstructure and interfaces of a reaction coating on aluminium alloys by laser processing

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# Microstructure and interfaces of a reaction coating on aluminium alloys by laser processing

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**Abstract** - This paper reports an approach to coat a ceramic layer on aluminium alloys by means of chemical reaction. The reaction product of $Al_2O_3$ layer of 100 μm in thickness has been formed using a powder mixture of silicon oxide and aluminium by laser processing. It turns out that the large amount of heat from the exothermic reaction has a predominate effects on the formation of the oxide layer. Further, the negative free energy of the reaction may promote the metal/oxide wetting. The micro-hardness and wear tests proved that the oxide layer is hard and strong. A mullite intermediate layer between aluminium and oxide have been identified by TEM. The atomic structure and defects of the reaction layer have been imaged at high resolution electron microscope.

## 1. INTRODUCTION

Hardfacing on Al alloys has been intensively investigated and widely used in order to extend Al alloys to the application of high wear resistance. Lately some attempts by means of laser to coat an intermetallic or a ceramic layer on the surface of Al alloys have been investigated[1,2]. However there are several difficulties in this process: (1) The high melting point of ceramics which is close to the boiling point of Al requires a high energy density of laser beam to melt ceramics which will generate a strong convection in the Al melt pool. This convection will cause surface roughness and may eventually destroy the coating; (2) The large difference of thermal expansion coefficient between Al (about 22 μm/m°C) and ceramics (mostly below 8 μm/m°C) will introduce high stresses at the metal/ceramics interface during rapid cooling which may cause failure of the interface bonding; (3) The rapid melting and solidification of laser process require a good wetting between liquid metal and solid ceramic within a very short period, say 0.1 second, however the wetting of Al on most ceramics is usually poor. Therefore it was pointed out[1] that laser coating on Al alloys is very difficult comparing with coating on other metals such iron-base. In order to overcome these drawbacks on the laser coating process, we have developed a novel approach mainly use chemical reaction[3]. In this reaction coating, a mixture powder of $SiO_2$ and Al was used to inject in the melt pool of Al heated by the laser beam. The reaction product of $\alpha$-$Al_2O_3$ layer in a thickness of 100 μm was formed and was mostly well bonded onto the Al surface. The micro-hardness of the layer is very high around $HV_{0.2}$ 2300 to 3060. A wear test demonstrated that there is no detectable wear from the coating. In this report a conventional transmission electron microscope and a high resolution electron microscope were used to study the microstructure and the interfaces in the reaction layer on Al alloys in order to have a better understanding of the structure and properties of the reaction coating.

## 2. EXPERIMENTS

To form a flat oxide layer, the laser coating parameters (CW-$CO_2$ Spectra Physics 820) were chosen with an output power of 1.0 -1.2 kw, the scan velocity 40 mm/s and defocus of 20 mm with a beam diameter of 3 mm. 67% overlap and 3 scans of coating have been applied in order to form a sufficient thickness of layer. A mixture powder of $SiO_2$ and Al with a mole ratio of 1:1 was injected into the laser melt pool of Al6061 substrate. The particle size ranged from 5 to 45 μm of Al powder and from 2 to 40 μm in the case of $SiO_2$. A relative smaller size of particles is favourable for a homogeneous reaction but because of aggregation of $SiO_2$ particles with Al makes it difficult to feed the mixing powders through the home-made powder feeding system. A JEM-200CX transmission electron microscope (TEM) operating at 200 kv and a high resolution electron microscope HREM (JEM-4000EX II) with a point-to-point resolution of 0.165 nm operating at 400 kV were used. Simulation of HREM images was carried out using the EMS program and Scherzer defocus was applied, where 10 nm of specimen thickness was used.

## 3. RESULTS AND DISCUSSION

The X-ray diffraction results from the reaction coating as shown in Fig.1 indicate that $\alpha$–$Al_2O_3$ is the predominant phase in the reaction layer. Silicon, mullite and crystalline $SiO_2$ also co-exist. Therefore the following chemical reaction has occurred: $2Al + 1/2SiO_2 = Al_2O_3 + 3/2Si$. According to SEM and EDX analyses, usually two interface layers exist between the reaction $\alpha$-$Al_2O_3$ coating and Al substrate as shown in Fig.2: one is the high silicon content layer bound with $\alpha$-$Al_2O_3$ and another is a thin layer with high Al-content contacted to the Al substrate. Based on this TEM and EDS results, the high silicon content layer is an amorphous silicate phase and the thin oxide layer located between the silicate and the Al substrate is mullite but not $Al_2O_3$ which is different from what we reported before[3]. According to the TEM and SEM observations, when two interface layers of silicate and mullite existed between the $\alpha$-$Al_2O_3$ coating and Al substrate, the interface of coating and substrate is always well bonded; if the interface consists only of $\alpha$-$Al_2O_3$ coating/Al substrate without mullite interlayer, failure sometimes occurred. Fig.3 illustrates a mullite interface layer between $SiO_2$ layer and Al substrate, where the bonding of metal/oxide and oxide/oxide is good. The HREM image of $Al_2O_3$ on [100] in Fig.4 demonstrates that a perfect crystal of $\alpha$-$Al_2O_3$ was formed in the reaction coating. The formation of perfect $\alpha$-$Al_2O_3$ crystals suggests that the reaction is very fast and that the properties of the reaction coating should be similar to that of sapphire. Fig.5 illustrates the HREM images of mullite on [010] direction. Comparison with the simulation images, where the 3:2 mullite ($3Al_2O_3.2SiO_2$)[4] was used, the defocus depths of the HREM image can be resolved. At the defocus of -84nm, a shift of atom columns in the HREM image, which is randomly distributed over the structure, can be observed. These atomic shifts suggest the presence of point defects in the mullite lattice. Atomic image of silicon precipitate on [110] demonstrates that (111) twin and stacking defects have been developed observed along [110] direction as shown in Fig.6, indicating that the coating heavily strained. As it is hard to observe an crystallographic orientation relationship between Al and mullite, an atomic image on both side of metal/oxide interface could not be obtained and the atomic arrangements in the vicinity of the interface are impossible to determine. Fig.7 represents an example of HREM image of Al[110]/mullite interface.

During laser processing of a ceramic layer on metals, wetting and interface strength between ceramic layer and metal substrate are two dominant properties. As the laser treatment is a rapid melting and solidification process, complete wetting of liquid metal to solid ceramic should be achieved in a very short period of time. The reason for requiring a complete wetting is because the metal/ceramic interface is rough. It seems to be possible to obtain this extreme only by a chemical reaction between the metal and oxide. According to the thermodynamic calculation of this reaction[3], the large negative free energy of -297 KJ/g.mole at 1173 °K, would significantly improve the wetting of metal on oxide. A large amount of heat of 383.4 kJ/g.mole released from the reaction, which can save up to 75% of laser energy, would melt the oxide completly. Usually enhanced wetting induces enhanced strength of the interface. Therefore

if the reaction product is strong and tough a well bonded ceramic coating might be formed on metals after laser treatment. It is known that the wetting of liquid Al on $Al_2O_3$ is poor below a certain temperature (about 950 °C); e.g. the wetting angle is 170° at 940 °C in Argon atmosphere. Therefore the coating on Al alloy with $Al_2O_3$ powder was not successful[3]. Similarly, as there is a high percentage of overlap between laser tracks, the reaction product of $Al_2O_3$ in the first laser track might not wet the liquid Al from the second track. Then cracks may occur along the $Al/Al_2O_3$ interface. However in this reaction coating a mullite intermediate layer was formed and may have good wetting with Al.

It is know that mullite[4] is a nonstoichiometric silicate compound with a wide variation of chemical composition, ranging from $3Al_2O_3.2SiO_2$ to $2Al_2O_3.SiO_2$. This nonstoichiometric behaviour and point defects of the mullite as identified by HREM might also be one reason for promoting wetting in this coating. For instance, the wetting angle can be improved[5] from 116° to 84° for $Cu/UO_2$ when the O/U ratio increased from 2.001 to 2.084, and from 120° to 0° for Cu/TiC when Ti/C ratio decreased from 1 to 0.5. Because of an extreme discontinuity in the dielectric properties across the metal-ceramic interface, the charged ions and defects in the ceramic may gain stability by proximity to the high dielectric metal. From classical image theory this stabilization energy is given as [6]:

$$U(z)=\rho\frac{Q^2}{4z\varepsilon_1}\frac{\varepsilon_1-\varepsilon_2}{\varepsilon_1+\varepsilon_2} \qquad (1)$$

where Q and ρ are the defect charge and defect density, z is the interfacial spacing, $\varepsilon_1$ and $\varepsilon_2$ are the dielectric constants of metal and ceramic. According to equation(1), adhesion is greater for the ceramic with high defect density and high charge of defects, like in mullite. Another interesting property of mullite is not subject to any polymorphic inversion or volume change. Therefore it exhibits a high thermal shock resistance[7]. It was reported[8] that reaction-bonded mullite ceramics exhibit a high fracture strength 290 MPa and that the volume expansion of the reactions almost compensates for the shrinkage on sintering. This superior ability of mullite to resist deformation[9] at high temperature might also help to prevent cracking along the interface. Therefore it may be concluded that the interface feature bonded by a mullite intermediate layer is one of the predominate reasons for the formation of a good bonding of oxide coating on Al alloy in this process.

## 4. CONCLUSIONS

A well bonded mullite intermediate layer between Al and oxide was identified by TEM. HREM images with a series of defocus demonstrated that a large amount of point defects existed in the mullite crystal. This mullite intermediate layer, which may promote wetting and adhesion between the metal and oxide, might be one of the predominate reasons for the formation of a strong reaction coating. Perfect crystallized $\alpha$-$Al_2O_3$, as well as twining and stacking defects in Si precipitates have been observed by HREM in the coating.

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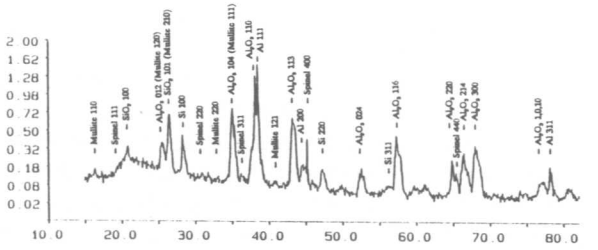



Fig.1 X-ray diffraction spectrum from the reaction coating on Al6061.

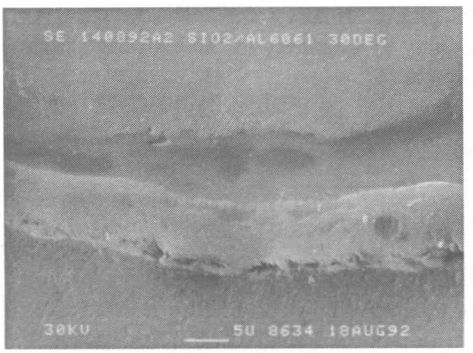



Fig.2 SEM picture from a cross-section of the reaction coating represents that two intermediate layers, a high Si -content oxide and a high Al-content oxide have been formed between the $\alpha$-$Al_2O_3$ coating and Al substrate.

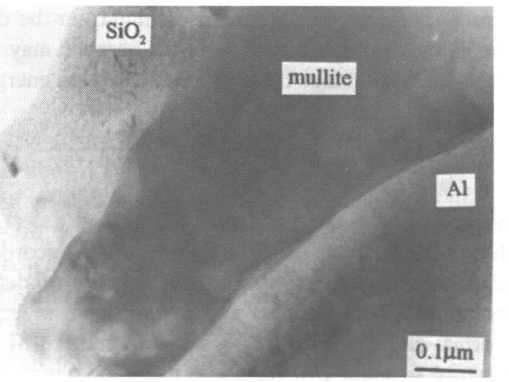
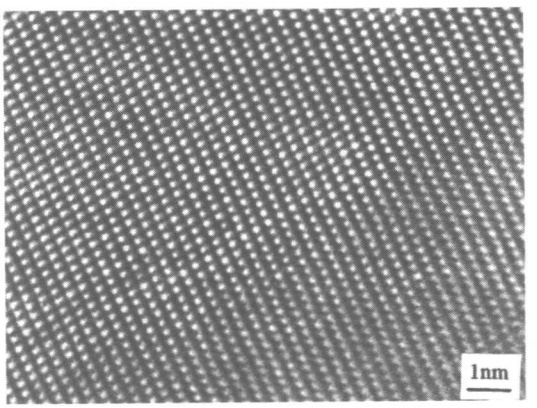



Fig.3 TEM micrograph illustrates a mullite interface layer between $SiO_2$ layer and Al substrate.



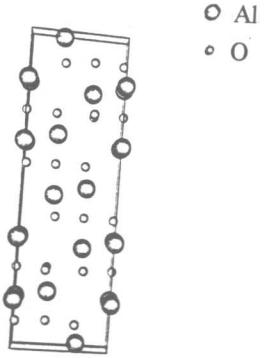




Fig.4 HREM image of $\alpha$-$Al_2O_3$ on [100] zone axis.

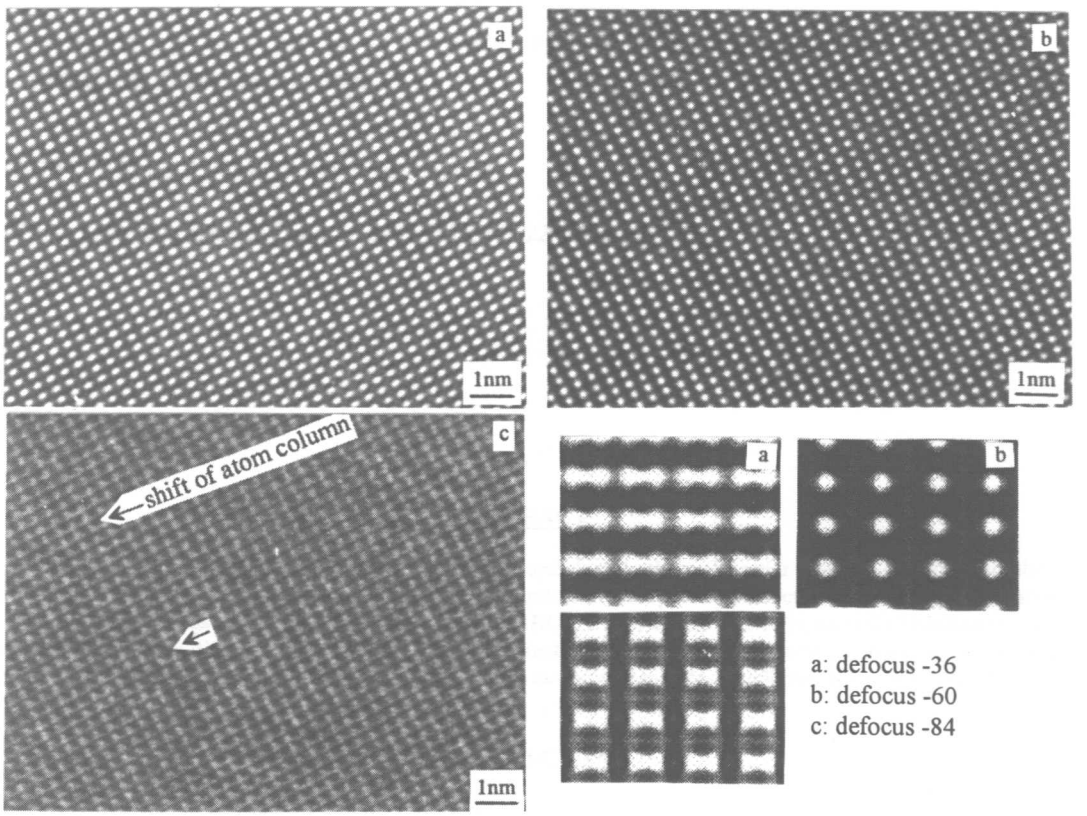



Fig.5 HREM images of mullite on [010] with a series of defocus and the relative simulation images.

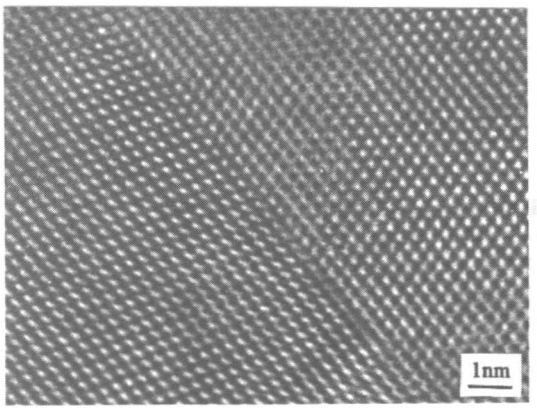



Fig.6 HREM image of Si precipitate on [110] demonstrates (111) twins and stacking defects.

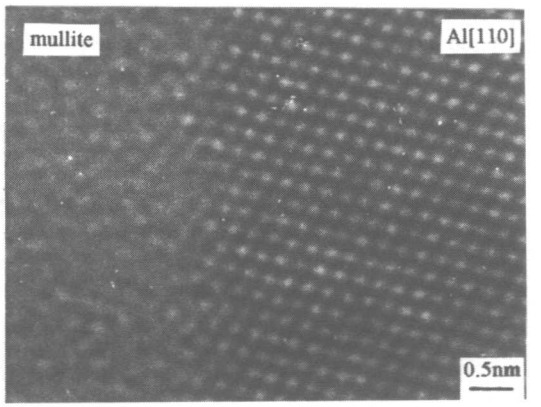



Fig.7 HREM image of Al[110]/mullite interface.